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CLIPPEDIMAGE= JP411102066A  
 PAT-NO: JP411102066A  
 DOCUMENT-IDENTIFIER: JP 11102066 A  
 TITLE: PLANOGRAPHIC PRINTING PLATE MATERIAL  
 PUBN-DATE: April 13, 1999

INVENTOR-INFORMATION:  
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 KUDO, SHINJI

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 NAME  
 COUNTRY  
 KONICA CORP  
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APPL-NO: JP09261914  
 APPL-DATE: September 26, 1997

INT-CL (IPC): G03F007/004; G03F007/004 ;  
 B41N001/14 ; G03F007/00

ABSTRACT:  
 PROBLEM TO BE SOLVED: To improve the shelf stability of a printing plate material and to ensure high sensitivity by forming a photosensitive layer contg. a compd. capable of generating acid when irradiated with active light, a compd. having a bonding part which can be decomposed by the acid, an IR absorber and an acid propagator on a substrate.

SOLUTION: A photosensitive layer contg. a compd. capable of generating acid when irradiated with active light, a compd.

29) 第3に、一般式(3)で表される有機酸エステルを挙げることもできる。

30]

一般式(3)

Al-5

Al-6

Al-7

Al-8

Al-9

20

\* 【0031】 式中、Zは前記と同義であり水素原子、C<sub>1</sub>～C<sub>8</sub>までのアルキル基又は示し、D<sub>2</sub>、D<sub>3</sub>はC<sub>1</sub>～C<sub>8</sub>までのアルキル基環状構造を形成するアルキレン或いは置換基を示す。

【0032】 この化合物は酸触媒によってカルボカチオンを形成し、水素移動しが発生するものと推定される。以下に、一表される有機酸エステルの具体例を挙げる。

【0033】

【化10】

410 PM

Some JP w/ SO<sub>3</sub>H gen from 7-22-01 spec.

all known in JP (not US)  
 But not w/ cl. Polymers!

【0017】  
【発明の実施の形態】式(I)及び(II)において、は環状アルキルであり、その炭素数は1~6程度でよい。Rで表されるアルキルとして具体的には、メチル、エチル、プロピル、イソプロピル、ブチル、イソブチル、ペンチル、ヘキシル等が挙げられる。

CLIPPEDIMAGE= JP408248561A

PAT-NO: JP408248561A

DOCUMENT-IDENTIFIER: JP 08248561 A

TITLE: PHOTOREACTIVE COMPOSITION,  
ACID-REACTIVE HIGH POLYMER COMPOSITION  
CONTAINING THE SAME AND ACID-REACTIVE RESIN  
LAYER

PUBN-DATE: September 27, 1996

## INVENTOR-INFORMATION:

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RES DEV CORP OF JAPAN

N/A

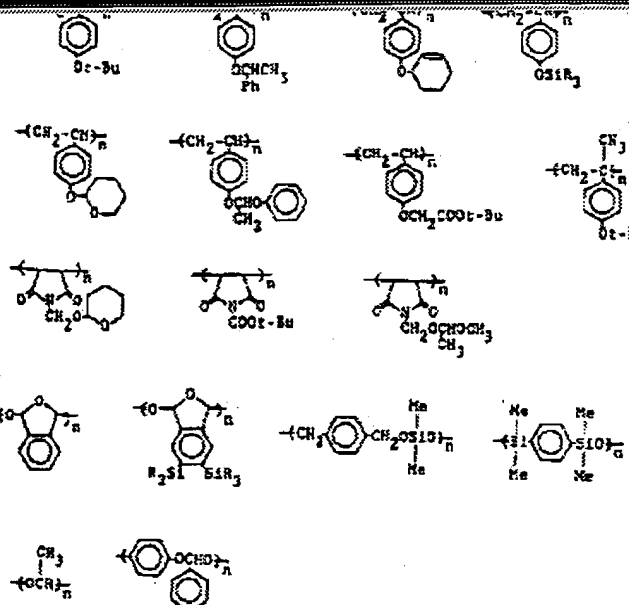
APPL-NO: JP07049588

APPL-DATE: March 9, 1995

INT-CL (IPC): G03C001/675; C08K005/15 ;  
C08K005/42 ; C08L025/18 ; C08L033/12

## ABSTRACT:

PURPOSE: To obtain a photoreactive composition having improved photosensing speed through amplifying photochemical reaction by using as the components of the composition, a photo-acid-generating agent that generates acid with the effect of light and an acid-breeding agent that newly generates acid with the acid generated by the photo-acid-generating agent.



2に、酸反応性低分子化合物を含有する  
ある。ここでは、酸反応性低分子化合物  
溶解性を低減する効果を有するものであ  
剤と呼ばれる。溶解抑制剤として、アセ  
ケタール化合物、カルボン酸の第3級エ  
ヒドロピラニルエステル、炭酸第3級エ  
ルキルシリル基やテトラヒドロピラニル  
フェノール類、ピナコール誘導体などを  
きる。これらの溶解抑制剤を含有する樹  
。たとえば、ノボラック樹脂、ポリ（p\*

\*-ヒドロキシステレン）、メタク  
30 メチロールマレイミド共重合体など  
る。低分子化合物はこれらの樹脂の  
する溶解性を阻害する効果を持つ  
ることによって、この溶解抑制効  
アルカリ可溶化となる。具体的な  
示す。

【0037】

【化14】

**\* NOTICES \***

**The Japanese Patent Office is not responsible for any damages caused by the use of this translation.**

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]**

[0001]

[Field of the Invention] this invention relates to the acid reactive polymer constituent and acid reactivity resin layer containing this photoreaction constituent further about the photoreaction constituent which raised the sensitization speed by combining the matter (it being hereafter called an acid propagation agent) which newly generates an acid with the generated acid with the matter (it being hereafter called a photo-oxide generating agent) which generates an acid in an operation of light.

[0002]

[Description of the Prior Art] A light energy is absorbed conventionally and it is used in the direction chemical between the molecules in a molecule or of various in the material which has the photosensitive function which produces a physical change. For example, it uses as an image formation material which detects optically the chemical structural change produced by the photoreaction, or in many fields, it is used and using as a surface-coating processing material which performs surface treatment etc. is put in practical use by optical hardening of a monomer or a prepolymer. However, the sensitization speed in the material which has these photosensitive functions, the sensitization wavelength field, and the definition are various, and the material which has a suitable property according to the purpose is chosen.

[0003] Although silver salt sensitive material was used more widely in ancient times as a material which has a photosensitive function, as in photoengraving-process technique etc., as extensive and a high-sensitivity image formation material which shows a high definition, the photopolymer which makes polymeric materials a principal component crosses broadly, and came (refer to the volume Yamaoka Tsugio and for Gentaro Matsunaga, "photopolymer technology", and Nikkan Kogyo Shimbun (1988)) to be used in recent years. The macromolecule system photosensitivity material is not only excellent in the definition, but can set up a wide range sensitization wavelength field by selection of the photoreaction. Moreover, it has many advantages of being able to manufacture comparatively cheaply. However, a sensitization speed is very low in comparing with a silver salt photosensitivity material, and the present condition is having not become 1/1000 of the sensitization speed which a silver salt material's shows, although it is called the high sensitivity macromolecule system photosensitivity material.

[0004] Until now, various attempts have been made in order to raise the sensitization speed of a macromolecule system photosensitivity material. It is the photopolymerization architecture to which having been most widely set as the object of a development makes an initiator the radical kind generated in an operation of light, and it carries out the polymerization of many vinyl monomers continuously. However, since the radical kind which reacts easily with the oxygen in air is a growth kind, it ends, without completing sufficient chain reaction. Moreover, with advance of a radical polymerization reaction, because of the network structure within the macromolecule matrix formed abruptly, a diffusion of a monomer is suppressed quickly and a polymerization cannot be completed. For such a cause, essential threshold value exists in the sensitization speed of a photopolymerization system.

[0005] On the other hand, the acid was generated in the operation of light and creation of various macromolecule system photosensitivity materials was attained by combining not only the cationic polymerization that makes this acid a catalyst but various acid catalyzed reactions. Although a high sensitivity is expected since there is no halt effect of the reaction by oxygen unlike a radical polymerization, the sensitization speed of present condition is rather lower in cationic polymerization, than a radical polymerization system in fact because of the moisture in air, or network-structure formation. Moreover, let it be a principle to heat-treat, after generating an acid with light, and to carry out the induction of the acid catalyzed reaction with the macromolecule system photosensitivity material incorporating the acid catalyzed reaction. For this reason, this kind that makes a photoresist the main use gestalt of macromolecule system photosensitivity material is called chemistry amplification type photoresist. However, still, the present condition was that a sensitization speed is a radical polymerization system, and it has been asked for the enhancement in a fast sensitization speed.

[0006] Furthermore, by combining using an optical radical polymerization and optical cationic polymerization \*\*\*\* or its both, the resin constituent which hardens a layer-like resin coat to a high degree of hardness by optical irradiation is also large liquefied, and practical use is presented. In recent years, the optical cationic polymerization system which does not receive the prevention effect by the oxygen in air is widely set as the object of development research, and although the development of the monomer and prepolymer suitable for the photo-oxide generating agent suitable for hardening or hardening is performed actively, it is asked for the enhancement in a cure rate for speeding up of a hardening process. Furthermore, in order that hardening of the resin constituent and the thick coat which the pigment which absorbs light distributed may happen only by the surface layer, the

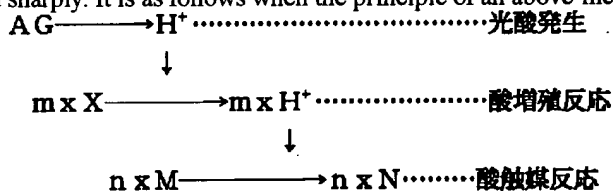
essential trouble where sufficient hardening is not brought has resulted as it is not solved. Moreover, it is also considered that it is considered for the base component of the minute amount which floats in air to bring a poisoning operation of a catalyst, or the acid catalyzed reaction in the inside of a macromolecule matrix triggers side reaction, and an acid catalyzed reaction stops as a cause by which it will not become so high although the sensitization speed of the above-mentioned chemistry amplification type photoresist uses the acid catalyzed reaction for this reason.

[0007]

[Problem(s) to be Solved by the Invention] By combining the matter which newly generates an acid with the acid generated to the matter which generates an acid in an operation of light as a result of this invention person's examining various the technique of solving such a situation radically, the photoreaction constituent which raised the sensitization speed remarkably is found out, it is what completed this invention and the purpose of this invention offers the photoreaction constituent which was made to amplify photochemical reaction and raised the sensitization speed remarkably.

[0008]

[Means for Solving the Problem] The photo-oxide generating agent in which the summary of invention of the 1st of this application generates an acid by operation of light, It is the photoreaction nature constituent which consists of an acid propagation agent which newly generates an acid with the acid generated from this photo-oxide generating agent. The photo-oxide generating agent which generates an acid by operation of light in the polymeric material which mixed the matter from which the summary of the 2nd invention produces molecular structure change by operation of an acid, or the polymeric material which combined the residue which produces molecular structure change by operation of an acid, It is the acid reactive polymer constituent characterized by making the acid propagation agent which newly generates an acid by operation of this acid exist. The polymeric material which mixed the matter from which the summary of the 3rd invention produces molecular structure change by operation of an acid, Or the acid propagation agent which newly generates an acid with the acid generated from the aforementioned photo-oxide generating agent in the resin layer which consists of a polymeric material which combined the residue which produces molecular structure change by operation of an acid, and a photo-oxide generating agent, The aforementioned resin layer which consists of a polymeric material which mixed the matter which produces molecular structure change by operation of the newly generated acid, or a polymeric material which combined the residue which produces molecular structure change by operation of an acid is an acid reactivity resin layer which has the two-layer structure which carried out the laminating of the different resin layer. Namely, by combining with a photo-oxide generating agent the acid propagation agent which newly generates an acid by operation of an acid in this invention Since one acid is generated, and this acid decomposes an acid propagation agent molecule and newly generates one or more acids from a photo-oxide generating agent by operation of light One or more acid-content children increase at one reaction, and it becomes a total of two or more acid-content children, and this reaction will arise continuously and occurrence's [ an acid ] will increase in \*\*\*\*\*. That is, by addition, a half of the acid catalyzed reaction by the alkali can also prevent the acid propagation agent with such a property, and disappearance of the acid by side reaction can also prevent it abruptly, as a result of [ its ] the increase of an acid, and an acid catalyzed reaction can be accelerated sharply. It is as follows when the principle of an above-mentioned reaction principle is illustrated.

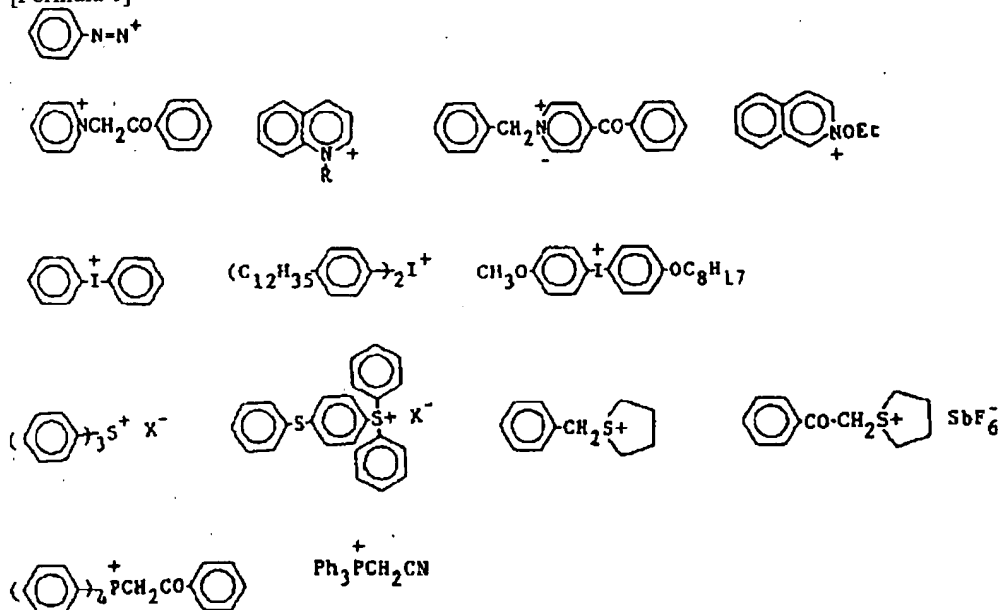


AG Photo-oxide generating agent; X an acid propagation agent --; M Acidolysis product; N The acidolysis products m and n are molecularities. The organic compound which increases such an acid was used, and the propagation reaction which generates an acid in \*\*\*\*\* was not known at all until now as an organic chemical reaction, although it was similar to a nuclear fission reaction or explosive reaction. Although it is thermally stable as much as possible, an acid decomposes and an acid propagation agent generates strong acid himself, it is the compound replaced by the residue of a comparatively strong acid, and triggers an elimination reaction comparatively easily and generates an acid. Therefore, if this elimination reaction can be sharply activated by the acid catalyzed reaction, although it is stable under un-existing of an acid, under presence of an acid, it becomes possible to make thermal reaction generate an acid easily. By combining the acid propagation agent with such a property with a photo-oxide generating agent, the photosensitive material whose sensitization speed improved by leaps and bounds became possible.

[0009] this invention is explained in detail. As a photo-oxide generating agent which generates an acid by operation of light in this invention, the compound used for a chemistry amplification type photoresist or optical cationic polymerization is used (" the volume on organic electronics material study group, imaging business an organic material refer to ", the \*\*\*\*\* exudation version (1993), and 187 - 192 pages). The example of the suitable compound for this invention is given to below. Moreover, in order to expand the sensitization wavelength field of these photo-oxide generating agents, a photosensitizer can also be made to live together suitably. With the acid active substance, the acid generated by the photolysis of these matter acts on an acid propagation agent, and promotes occurrence of an acid. The following photo-oxide generating agents can be used. PF6- of aromatic onium compounds, such as a diazonium, ammonium, iodonium, sulfonium, and a phosphonium, AsF6-, SbF6-, and a CF3SO3-salt can be mentioned [ 1st ]. The concrete example of an onium compound is shown below.

[0010]

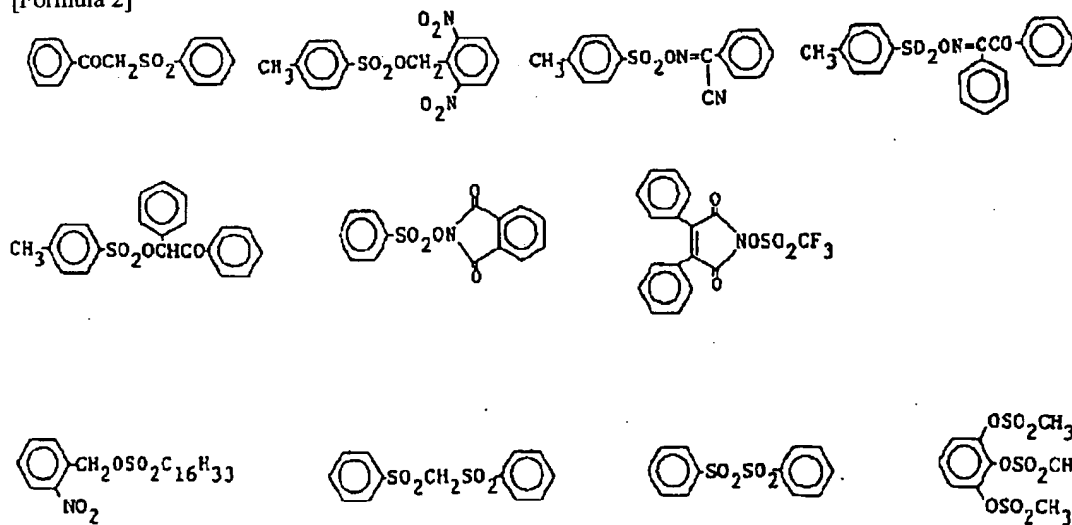
[Formula 1]



[0011] The sulfonation object which generates [ 2nd ] a sulfonic acid can be mentioned. A concrete compound is illustrated below.

[0012]

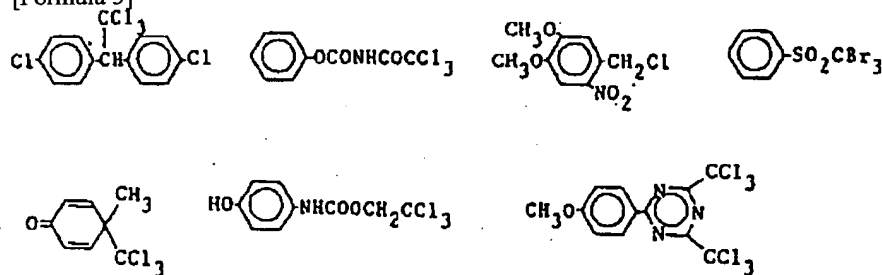
[Formula 2]



[0013] The halogenide which carries out the optical occurrence of the hydrogen halide can also be used [ 3rd ]. A concrete compound is illustrated below.

[0014]

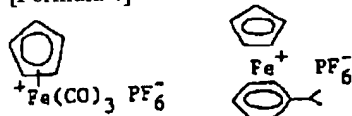
[Formula 3]



[0015] An iron allene complex can be mentioned to the 4th.

[0016]

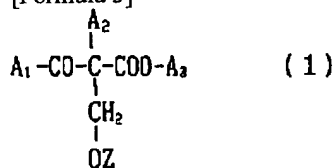
[Formula 4]



[0017] The acid propagation agent used by this invention is the compound replaced by the residue of a comparatively strong acid, and is a compound which triggers an elimination reaction comparatively easily and generates an acid. Therefore, this elimination reaction can be sharply activated by the acid catalyzed reaction, and although it is stable under un-existing of an acid, under presence of an acid, it becomes possible easily to make an acid generate according to thermal reaction. By combining the acid propagation agent with such a property with a photo-oxide generating agent, the photoreaction nature constituent whose sensitization speed improved by leaps and bounds became possible. An acid catalyzed reaction decomposes and an acid (it is ZOH at the following general formulas) is generated again. One or more acids are increasing in number at one reaction, and a reaction progresses in acceleration in connection with advance of a reaction. In order for the generated acid itself to carry out the induction of the autolysis, the intensity of the acid generated here is set to an acid dissociation constant and pKa, and is three or less, and it is desirable that it is two especially or less. An autolysis cannot be caused if it is an acid weaker than this. As such an acid, a dichloroacetic acid, a trichloroacetic acid, a methanesulfonic acid, ethane sulfonic acid, a benzenesulfonic acid, p-toluenesulfonic acid, a naphthalene sulfonic acid, a triphenyl \*\*\*\*\* acid, etc. can be raised. Specifically, the following compounds can be illustrated. The organic-acid ester compound expressed [ 1st ] with a general formula (1) can be mentioned.

[0018]

[Formula 5]

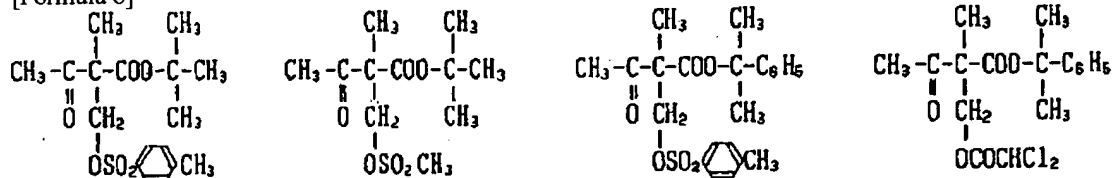


[0019] (A1 shows the alkyl group or aryl group from C1 to C6 among a formula, A2 shows the alkyl group from C1 to C6, and A3 is a screw (p-alkoxy phenyl) methyl) A machine, a 2-alkyl-2-propyl group, a 2-aryl-2-propyl group, a cyclohexyl machine, or a tetrahydropyranyl group is shown, and Z shows the residue of the acid shown by ZOH whose acid dissociation constant (pKa) is three or less.

If an acid acts on this compound, an ester machine decomposes and it becomes a carboxylic acid, and after this starts a \*\* carboxylic acid further, an acid (ZOH) will \*\*\*\* easily. Specifically, an example is shown below.

[0020]

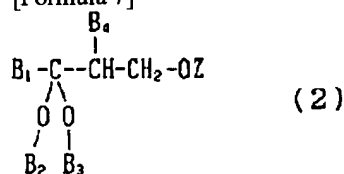
[Formula 6]



[0021] The organic-acid ester with the acetal or ketal machine expressed [ 2nd ] with a general formula (2) can be mentioned.

[0022]

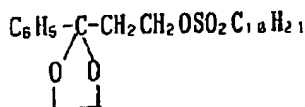
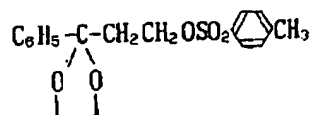
[Formula 7]



[0023] (Z has the same meaning as the above among a formula, B1 is a hydrogen atom, an alkyl group, or an aryl group, B-2 and B3 form ethylene or a propylene machine in a methyl, an ethyl group, or both, and B4 shows a hydrogen atom or a methyl group) An acetal or a ketal decomposes in an operation of an acid, this compound serves as beta-aldehyde or a ketone, and ZOH is easily desorbed from it after this. A concrete example is shown below.

[0024]

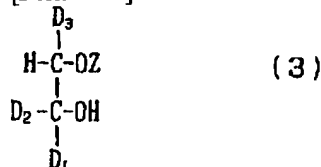
[Formula 8]



[0025] The organic-acid ester expressed [ 3rd ] with a general formula (3) can be mentioned.

[0026]

[Formula 9]

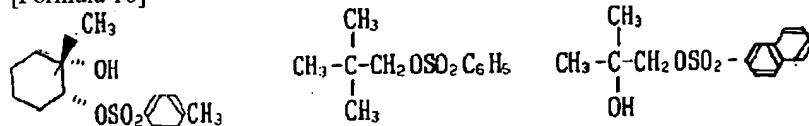


[0027] (Z has the same meaning as the above among a formula, D1 and D2 show a hydrogen atom, the alkyl groups from C1 to C6, or an aryl group, and D2 and D3 show the alkylene or substitute alkylene residue which forms alicycle-like structure on the alkyl group or both sides from C1 to C6)

A hydroxyl group \*\*\*\*\* by the acid catalyst, and after this compound forms and carries out the hydrogen move of the carbocation, it is presumed to be what ZOH generates. A concrete example is shown below.

[0028]

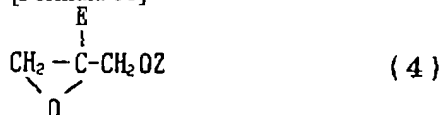
[Formula 10]



[0029] The organic-acid ester which has the epoxy ring expressed [ 4th ] with a general formula (4) can be mentioned.

[0030]

[Formula 11]

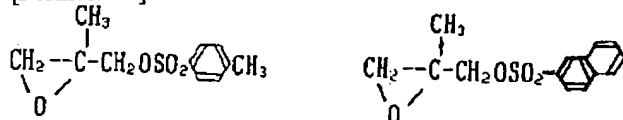


[0031] (Z has the same meaning as the above among a formula, and E shows the alkyl groups or phenyl groups from C1 to C6)

If an acid acts on this compound, a cation will be formed in beta-carbon in connection with generation of the ring breakage of an epoxy ring, and what an organic acid generates as a result which is a hydrogen move will be presumed. A concrete example is shown below.

[0032]

[Formula 12]



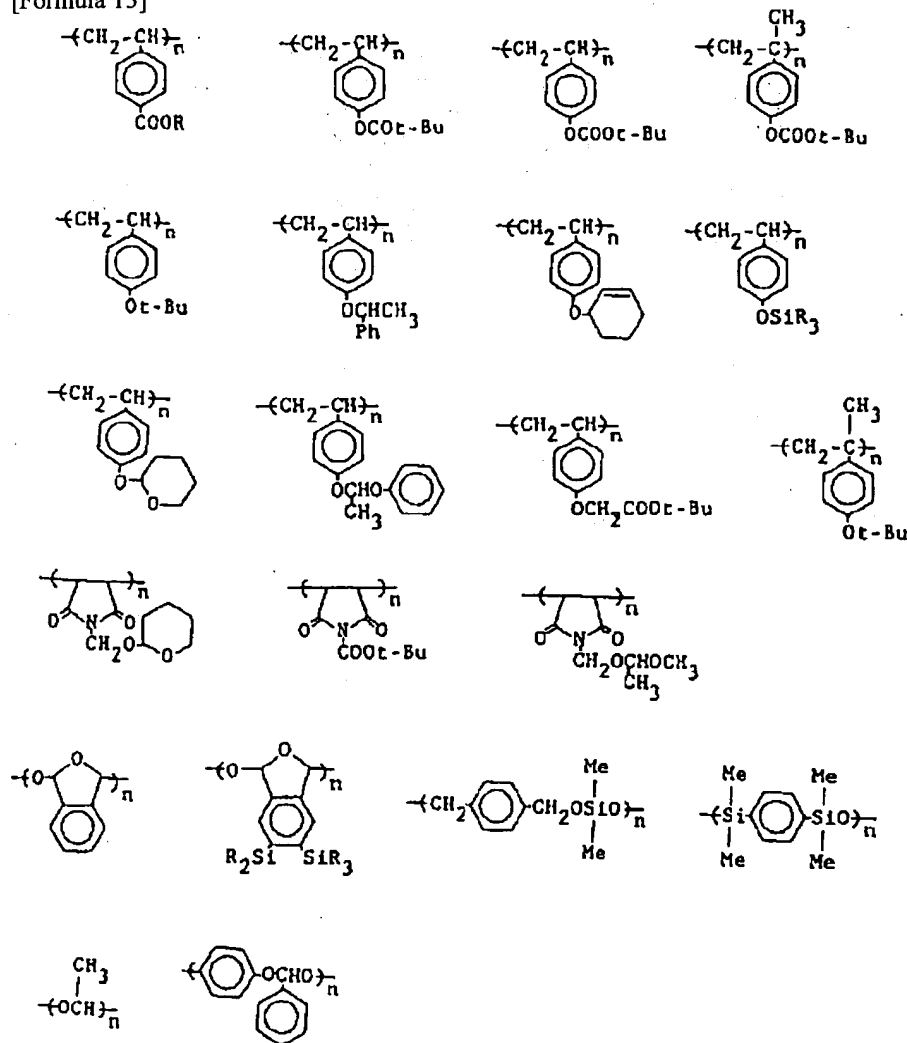
[0033] These compounds exist stably at a room temperature, unless an acid acts. Although the acid strength more than fixed is needed in order to cause acid-catalyst disassembly of these compounds, it is desirable that it is about two or less in an acid dissociation constant pka. If it is the acid dissociation constant beyond this, i.e., an acid weak more than this, the reaction of an acid propagation agent cannot be triggered.

[0034] Next, the polymeric material which mixed the matter (acid reactivity molecule) which produces molecular structure change by operation of the acid in which the above-mentioned photoreaction constituent is made to exist, or the polymeric material which combined the residue which produces molecular structure change by operation of an acid is explained. In addition, the matter or residue which produces molecular structure change is only called an acid reactivity molecule or acid reactivity residue. The example of a polymeric material which mixes, or joins together and becomes about the acid reactivity molecule used



suitable for this invention is shown ("the volume on organic electronics material study group, imaging business an organic material refer to", the \*\*\*\* exudation version (1993), and 199 - 201 pages). many use the reaction of the deprotection machine in an organic synthetic chemistry -- \*\*\*\* (T. refer to W. Greene, Protective Groups in Organic Synthesis, and John Wiley & Sons (1981)) -- a concrete example is shown below The polymeric material which has an acid reactivity residue in a side chain or a principal chain can be mentioned to the 1st. As an acid reactivity residue, the phenol nature or N-methylol nature hydroxyl group protected by the 2nd class, the 3rd class ester, the tetrahydropyranyl ester, the 3rd class ester of carbonic acid, the trialkylsilyl group, and tetrahydropyranyl group of a carboxylic acid is used suitably. Since a deprotection reaction happens and a polar high carboxylic acid and polar high phenol generate these by operation of an acid, the exposure section is solubilized in a polar solvent or an alkaline-water solution. There is high-sensitivity sensitive material as a thing using such a property. As an example of a concrete compound, it is [0035].

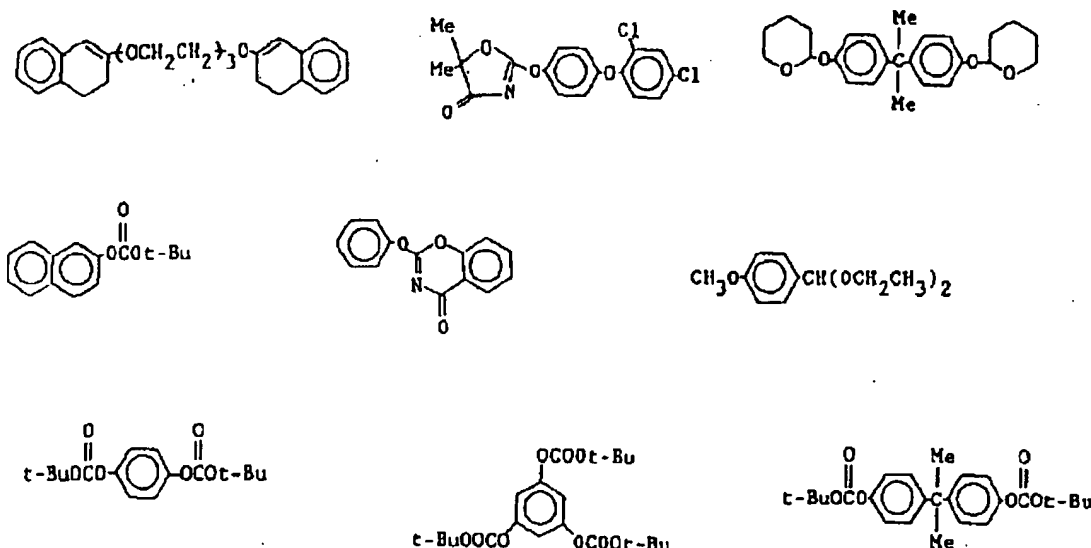
[Formula 13]



[0036] The high molecular compound containing an acid reactivity low molecular weight compound is in the 2nd. Here, an acid reactivity low molecular weight compound has the effect of reducing the solubility of a resin compound, and is called dissolution inhibitor. As a dissolution inhibitor, a phenols, a pinacol derivative, etc. which were protected by an acetal compound, a ketal compound, the 3rd class ester of a carboxylic acid, tetrahydropyranyl ester, the 3rd class ester of carbonic acid, the trialkylsilyl group, or the tetrahydropyranyl group can be mentioned. As a resin compound containing these dissolution inhibitors, a novolak resin, poly (p-hydroxy styrene), a methacrylic-acid copolymer, N-methylol maleimide copolymer, etc. can be raised. Although a low molecular weight compound has the effect which checks the solubility over the alkaline-water solution of these resins, by decomposing in an operation of an acid, this lysis depressor effect is lost and a macromolecule serves as alkali solubilization. A concrete dissolution inhibitor is illustrated below.

[0037]

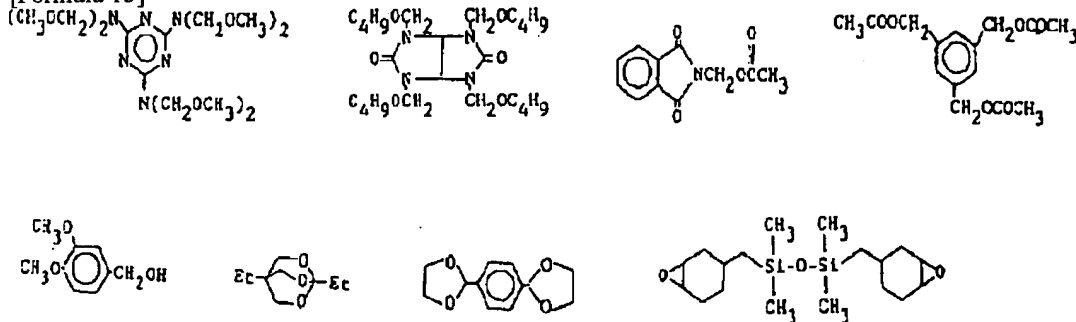
[Formula 14]



[0038] The condensation reaction by the acid catalyzed reaction is used [ 3rd ] for the crosslinking reaction of a macromolecule. As a residue which forms a cation and starts a condensation reaction by the acid catalyst, a benzyl alcohol derivative, a melamine derivative, N-methylol imide derivative, an acetal derivative, a vinyl ether derivative, etc. can be raised. Moreover, as a residue which reacts with generated \*\*\*\*\*, phenol, alcohol, etc. can be mentioned and polymer \*\* of the macromolecule which has these residues, for example, the polymer of p-hydroxy styrene, a novolak resin, and hydroxyethyl methacrylate is used suitably. The compound which starts a condensation reaction is illustrated below.

[0039]

[Formula 15]



[0040] Moreover, since the macromolecule having this condensation nature residue and the phenyl residue causes bridge formation by the acid catalyst by itself, it is convenient to this invention. The macromolecule with the residue which carries out 4th ] a polymerization by the acid catalyst is used. As a cationic polymerization nature residue, an epoxy group, an oxetane residue, a vinyl ether machine, an isopropenyl phenyl group, annular orthochromatic ester, etc. can be raised. The constituent set to the 5th from a cationic polymerization nature monomer or a prepolymer is also used. As a cation nature monomer unit, an epoxy group, an oxetane machine, a vinyl ether machine, and annular orthochromatic ester are used. It is desirable to carry out the mixing of these monomers or prepolymers to a vinyl system polymer, and to consider as the filmy material of self-support nature.

[0041] Subsequently, the adjustment technique of the photopolymer constituent of this invention is described below. To the high molecular compound which is acid reactivity, the resin or itself containing the low-molecular matter with an acid reactivity unit adds 0.5 - 20% of the weight of a photo-oxide generating agent, and 0.1 - 20% of the weight of an acid propagation agent to it. Since many of above-mentioned photo-oxide generating agents generate a radical kind with an acid, it can also carry out the mixing of a radical polymerization nature monomer or the prepolymer with the acid active substance. Furthermore, you may add a pigment, a color, etc. suitably.

[0042] In order to distribute uniformly, it is desirable to melt each liquefied. It exposes, after making these constituents into the shape of a layer, and the acid as a latent image is generated. Subsequently, while heating (postbake) processing is performed and urging to a chain of decomposition of an acid propagation agent, an acid catalyzed reaction causes a structural change of the acid active substance. although the conditions of heat-treatment are changed according to the activity modality of residue, the modality of macromolecule, etc. in exposure energy and the acid to use -- heating temperature -- the domain of 60 to 150 degrees -- it is the domain of 80 to 130 degrees more preferably A heating time is 5 minutes from 30 seconds more preferably from 10 seconds for 10 minutes. If a heating time is short more than this, an acid catalyzed reaction will not fully be triggered, in time to exceed this domain, an acid propagation agent may trigger side reaction, and a productivity is missing. The resin or itself containing the acid active substance uses change of the physical properties before and behind the exposure accompanied by a structural change of the

resin which is acid reactivity, and heat-treatment, for example, solubility, a degree of hardness, a thickness, viscosity, gassing, etc. Furthermore, it can divide into the resin layer which contains a photo-oxide generating agent in this invention, and the resin layer containing an acid propagation agent, and can consider as two-layer structure. Next, this invention is explained still concretely with an example.

[0043]

[Example] The synthetic example of the typical acid propagation agent which can be first used by this invention is shown as an example of reference.

It was made to react to the 2-methyl-3-keto butanoic-acid tert butyl ester which example of reference 1 acetoacetic-acid tert-butyl ester was made to react with a methyl iodide, and obtained it under presence of the sodium hydride in THF with formalin in ethanol under presence of a potassium hydroxide. The 2-hydroxymethyl-2-methyl-3-keto butanoic-acid tert butyl ester generated at 40% of yield was made to react with p-tosyl chloride under presence of a triethylamine in a dichloromethane, and 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic-acid tert butyl ester was obtained as oily matter. The product was refined by silica gel column chromatography -

m. p.52-53 degree-C<sup>1</sup>H-NMR (CDCl<sub>3</sub>)

delta(ppm): 1.38 (s, 3H, -COC(CH<sub>3</sub>) CO-), 1.40 (s, 9H, -C<sub>3</sub> (CH<sub>3</sub>)), 2.15 (s, 3H, and CH<sub>3</sub>CO-), 2.47 (s, 3H, Ar-CH<sub>3</sub>), 4.28 (ABq, J= 10Hz, 2H, and -CH<sub>2</sub>-OSO<sub>2</sub>-), 7.38 (d, J= 7.7Hz, 2H, Ar-H), 7.77 (d, J= 7.7Hz, 2H, Ar-H)

IR(cm<sup>-1</sup>): 3000, 1738 (>C=O of ester), 1719 (>C=O)

Elemental-analysis C<sub>17</sub>H<sub>24</sub>O<sub>6</sub>Scalc. C:57.29% H:6.79% S:9.00%found C:57.18% H:6.90% S:8.84% [0044] A methanesulfonyl acid chloride is used instead of p-tosyl chloride like example of reference 2 example 1, and it is 2-methyl-2-Methane sulfonyl oxy-3-keto butanoic-acid tert butyl ester was obtained as oily matter.

<sup>1</sup>H-NMR(CDCl<sub>3</sub>)

delta(ppm): 1.50 (s, 12H, -C<sub>3</sub> (CH<sub>3</sub>)), -COC(CH<sub>3</sub>) CO-, 2.22 (s, 3H, and CH<sub>3</sub>CO-), 3.05 (s, 3H, -OSO<sub>2</sub>CH<sub>3</sub>), 4.50 (s, 2H, and -CH<sub>2</sub>-OSO<sub>2</sub>-)

<sup>13</sup>C-NMR(CDCl<sub>3</sub>)

delta(ppm): 17.2 (CH<sub>3</sub>), 27.2 (CH<sub>3</sub>), 27.5 (CH<sub>3</sub>), 36.9 (CH<sub>3</sub>), 59.9 (> C<), 71.1 (> C<), 83.1 (CH<sub>2</sub>), 168.3 (C=O), 202.7 (C=O)

IR(cm<sup>-1</sup>): 2981, 1738 (>C=O of ester), 1714 (>C=O)

Elemental-analysis C<sub>11</sub>H<sub>20</sub>O<sub>4</sub>Scalc. C:47.13% H:7.19% S:11.44%found C:47.33% H:7.45% It was made to react with 2-phenyl-2-propanol, having used sodium acetate as the catalyst, and example of S:10.3% reference 3 diketene was made into acetoacetic-acid 2-phenyl-2-propyl ester. The hydroxymethyl derivative which performs methylation and methylol-ization like an example 1 and was obtained in this was made to react with p-tosyl chloride, and 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic-acid 2-phenyl-2-propyl ester was obtained as oily matter.

<sup>1</sup>H-NMR(CDCl<sub>3</sub>)

delta(ppm): 1.39 (s, 3H, -COC(CH<sub>3</sub>) CO-), 1.75 (s, 3H, -O-C(CH<sub>3</sub>)<sub>2</sub>-), 1.79 (s, 3H, -O-C(CH<sub>3</sub>)<sub>2</sub>-), 2.12 (s, 3H, and CH<sub>3</sub>CO-), 2.44 (s, 3H, Ar-CH<sub>3</sub>), 4.30 (ABq, J= 14Hz, 2H, and -CH<sub>2</sub>-OSO<sub>2</sub>-), 7.30 (s, 5H, Ar-H), 7.35 (d, J= 8.7Hz, 2H, Ar-H), 7.74 (d, J= 8.7Hz, 2H, Ar-H)

IR(cm<sup>-1</sup>): 2983, 1738 (>C=O of ester), 1716 (>C=O)

Elemental-analysis C<sub>22</sub>H<sub>26</sub>O<sub>6</sub>Scalc. C:63.14% H:6.26% S:7.66%found C:62.98% H:6.48% S:7.76% [0045] The methylol-ized acetoacetic-acid 2-phenyl-2-propyl ester which was obtained in the example of reference 4 example 3 is made to react with methane sulfonyl chloride, and it is [oxy-/ 2-methyl-2-methane sulfonyl ]. -3-keto butanoic-acid 2-phenyl-2-propyl ester was obtained as oily matter.

<sup>1</sup>H-NMR(CDCl<sub>3</sub>)

delta(ppm): 1.49 (s, 3H, -COC(CH<sub>3</sub>) CO-), 1.75 (s, 3H, -O-C(CH<sub>3</sub>)<sub>2</sub>-), 1.80 (s, 3H, -O-C(CH<sub>3</sub>)<sub>2</sub>-), 2.20 (s, 3H, and CH<sub>3</sub>CO-), 2.90 (s, 3H, -SO<sub>2</sub>CH<sub>3</sub>), 4.48 (dd, J= 13Hz, 2H, and -CH<sub>2</sub>-O-), 7.30 (s, 5H, Ar-H)

IR: 2985, 1738 (>C=O of ester), 1714 (>C=O)

The example of reference 5 1-methyl hexene was oxidized under presence of osmium <8> oxide, and the cis--1-methyl 1 and 2-dihydroxy hexane were obtained. This was made to react under presence of p-tosyl chloride and a triethylamine, and the cis--1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane was obtained at 82% of yield.

Colorless prism \*\* m.p.65-66 degree-CIR (KBr) 3460, 2935, 1598, and 1348, 1176cm<sup>-1</sup>, <sup>1</sup>H-NMR(60MHz, CDCl<sub>3</sub>) delta=1.1 (s, and 3H and -CCH<sub>3</sub> (OH)-), 1.9 (s, 1H, OH), 1.1-2.0 (m, 8H, -(CH<sub>2</sub>)<sub>4</sub>-), 2.5 (s, 3H, Ar-CH<sub>3</sub>), 4.3 (ABq, 1H, and -CH(OTs)-, J= 5, 9Hz), 7.4 (d, 2H, Ar-H, J= 8Hz), 7.8 (d, 2H, Ar-H, J= 8Hz)

[0046] The example of reference 6 2-methyl-3-hydroxy propene was oxidized by tert-butyl hydroperoxide under presence of a triphenyl phosphine, and the 1 and 2-epoxy-2-methyl-3-hydroxy propane was obtained. This was made to react with p-tosyl chloride under presence of a triethylamine, and the 1 and 2-epoxy-2-methyl-3-(p-toluenesulfonyloxy) propane was obtained. Colorless oily matter IR (NaCl) 1600, 1364, and 1192, 1178cm<sup>-1</sup><sup>1</sup>H-NMR(60MHz, CDCl<sub>3</sub>) delta=1.3 (s, 3H, CH<sub>3</sub>), 2.5 (s, 3H, Ar-CH<sub>3</sub>), 2.9 (s, 2H, and -CH<sub>2</sub>O-), 7.4 (d, 2H, Ar-H, J= 8Hz), 7.8 (d, 2H, Ar-H, J= 8Hz)

After ketal-izing example of reference 7 benzoylacetic-acid ethyl ester by ethylene \*\*\*\*\*, it returned with lithium-hydride aluminum and considered as the 3-phenyl -3 and 3-ethylene dioxy propanol -1. p-tosyl chloride was made to react to this under presence of a triethylamine, and the crystalline 1-(p-toluenesulfonyloxy)-3-phenyl -3 and 3-ethylene dioxy propane were obtained with about 70% of yield.

Colorless oily matter m.p.48-50 degree-CIR (KBr) 2892, 1597, and 1354, 1178cm<sup>-1</sup>, <sup>1</sup>H-NMR(90MHz, CDCl<sub>3</sub>) delta=2.27 (t, 2H, and -CH<sub>2</sub>CH<sub>2</sub>OTs, J= 8Hz), 2.44 (s, 3H, Ar-CH<sub>3</sub>) and 3.6- 4.1 (m, 4H, and -OCH<sub>2</sub>CH<sub>2</sub>O-), 4.15 (t, 2H, and -CH<sub>2</sub>CH<sub>2</sub>OTs, J= 8Hz), and 7.2- 7.5 (m, 7H, Ar-H) and 7.76 (d, 2H, Ar-H, J= 8Hz)

[0047] The 4 % of the weight cyclohexane solution of example 1 poly (p-(tert-butoxycarbonyloxy) styrene) was prepared, and the diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate which is 5% of the weight (it is two mol % to a monomer unit) of a photo-oxide generating agent was melted to this polymer. Addition of the 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic-acid tert butyl ester which is the acid propagation agent obtained in the example 1 of reference in this solution was carried out to this polymer 10% of the weight (it is six mol % to a monomer unit). It considered as the thin film which carries out the spin application of this solution on a silicon wafer, and has a 0.5-micrometer thickness, and prebake processing was performed for this for 1 minute at 100 degrees C. For the comparison, the poly membrane which does not contain an acid propagation agent was prepared similarly. These poly membranes were drawn for 7 minutes, and after changing time and carrying out the UV irradiation of each, postbake processing was performed at 100 degrees C. Since the acid decomposed and the thickness reduced this macromolecule, it measured thickness change and evaluated the sensitization speed. By the postbake for 2 minutes, in the acid propagation agent additive-free case, the decrement in a thickness was about about 25% in the exposure for 17 seconds to the acidolysis of a macromolecule being completed by exposure for 17 seconds, when an acid amplification agent is added, and in order to melt completely, the exposure for 50 seconds was required. Moreover, when an acid propagation agent was added, the decrement of the thickness in a postbake has happened abruptly and the amplification effect accepted clearly. Image formation was checked by carrying out postbake processing behind the bottom of exposure through a mask.

[0048] Instead of the diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate used as a photo-oxide generating agent in example 2 example 1, 6% of the weight of 2 and a 3-diphenyl-3-keto-2-hydroxy-1-(p-toluenesulfonyloxy) propane were added as a photo-oxide generating agent, and the addition effect of the 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic-acid tert butyl ester obtained in the example 1 of reference was investigated. The postbake was performed at 100 degrees C for 3 minutes after carrying out the spin application of the thin film on a silicon wafer like an example 1 and carrying out ultraviolet-rays exposure. In the acid propagation agent additive-free case, although the decrement of the thickness containing an acid propagation agent was abruptly completed by the exposure for 60 seconds, the thickness decreased only about 15%, but in order to complete a thickness decrement, it required the exposure time for 180 seconds at the same exposure time.

The 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic-acid tert butyl ester which is 3.4% of the weight of triphenylsulfonium triflate and 1% of the weight of an acid propagation agent was added to the cyclohexane solution of a polymer used in the example 3 example 1 to the polymer, and the thin film was prepared. After exposing ultraviolet rays, when the postbake was performed at 100 degrees C for 3 minutes, the decrement in a thickness was completed by the exposure for 55 seconds. In order in an additive-free case to remain in the decrement of about 15% of a thickness at the same exposure time and to complete an acid propagation agent, the exposure time for 150 seconds was required.

[0049] The cis--1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane obtained to the polymer in the cyclohexane solution of a polymer used in the example 4 example 1 in 10% of the weight of diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate and the example 5 of reference was added 5% of the weight, and on the silicon wafer, the spin application was carried out and it considered as the 0.5-micrometer thin film. After performing a postbake for 2 minutes at 100 degrees C after exposing ultraviolet rays, negatives were developed by ethanol, and \*\*\*\* was measured. Although all layers melted by the exposure time for 10 seconds when an acid propagation agent was added, the exposure time for 70 seconds or more was required of additive-free. The 1 and 2-epoxy-2-methyl-3-hydroxy propane compounded in the example 6 of reference instead of the cis--1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane used in example 5 example 4 was added. The exposure time required when a UV irradiation, postbake processing, and ethanol development are performed similarly, in order to melt all layers by adding an acid propagation agent was able to be shortened to the quadrant.

[0050] The cis--1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane obtained in 10% of the weight of diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate and the example 5 of reference was added to 2:1 copolymers (Mw=4.01x10<sup>4</sup>, Mw/Mn=1.74) of example 6 methyl methacrylate and methacrylic-acid 2-phenyl-2-propyl ester 5% of the weight, and on the silicon wafer, the spin application was carried out and it considered as the 0.23-micrometer thin film. After irradiating ultraviolet rays at this, postbake processing was performed for 2 minutes at 100 degrees C, negatives were developed by ethanol, and the remaining rate of membrane was measured. By adding an acid propagation agent, the exposure time required for becoming a \*\*\*\* zero was able to be shortened to the quadrant.

The same exposure, a postbake, and ethanol development were performed using the 1-(p-toluenesulfonyloxy)-3-phenyl -3 and 3-ethylene dioxy propane which were compounded in the example 7 of reference instead of the cis--1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane used in example 7 example 6. By adding this acid propagation agent, the exposure time for solubilizing all layers was able to be shortened to about 1/3.

[0051] In the cyclohexanone solution of a polymer used in the example 8 example 1, the diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate which is a photo-oxide generating agent, and the 1-(p-toluenesulfonyloxy)-3-phenyl -3 and 3-ethylene dioxy propane were added 10% of the weight to the polymer, respectively, and on the silicon wafer of three sheets, the spin application was carried out, respectively and it considered as the 0.25-micrometer thin film. After irradiating ultraviolet rays through the fenestera rotunda with a diameter of 3mm at these thin films, it heat-treated at 105 degrees C, 115 degrees C, and 125 degrees C. After the stain accompanied by the decrement in a thickness appeared immediately as a round shape which is 3mm, the round shape increased with time. Postbake time until a diameter is set to 12mm was 30 seconds by 125 degrees C for 45 seconds

at 115 degrees C in 105 degrees C for 7 minutes. This is because the acid generated with light is spread by heating within a poly membrane and the acid occurrence by decomposition of an acid propagation agent is caused one after another in connection with it. When an acid propagation agent was not added, such a decrement did not happen.

[0052] % of the 15 mol 1-(p-toluenesulfonyloxy)-3-phenyl -3 as two mol % of 2, and a 3-diphenyl-3-keto-2-hydroxy-1-(p-\*\*\*\*\*)) propane and an acid propagation agent as a photo-oxide generating agent and 3-ethylene dioxy propane were added to the solution of 2-methoxy ethyl acetate of an example 9p-trimethyl silyloxy styrene homopolymer ( $5.35 \times 10^4$ ,  $M_w/M_n=1.69$ ). After it carried out the spin application of this solution by 1000rpm and it carried out the prebake for 30 seconds at 100 degrees C on the silicon wafer, time was changed, ultraviolet rays were irradiated and the postbake was given for 30 seconds at 100 degrees C. When it was immersed for 10 seconds into ethanol and negatives were developed, the exposure time which a poly membrane solubilizes completely was shortened to about 1/3 compared with acid propagation agent additive-free.

After adding 3% of the weight of diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate, and 3% of the weight of 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic-acid tert butyl ester to the cyclohexane solution of 1:1 copolymers ( $M_w=5.15 \times 10^4$ ,  $M_w/M_n=2.04$ ) of example 10 methyl methacrylate and a glycidyl methacrylate to this polymer, the spin application was carried out on the anodic oxidation aluminum plate. To this, time was changed, ultraviolet rays were exposed, and after carrying out the postbake at 100 degrees C for 3 minutes, the plate was washed with toluene. When compared with the case where an acid propagation agent is not added, the exposure time which insolubilization of a copolymer takes was shortened to 1/5.

[0053] Addition of the 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic-acid tert butyl ester which is the acid propagation agent obtained in the example 1 of reference in the cyclohexane solution of a polymer used in the example 11 example 1 was carried out to this polymer 10% of the weight (it is six mol % to a monomer unit). It considered as the thin film which carries out the spin application of this solution on a silicon wafer, and has a 0.27-micrometer thickness, and prebake processing was performed for this for 1 minute at 100 degrees C. For the comparison, the poly membrane which does not contain an acid propagation agent was prepared similarly. 3.5% of the weight of triphenylsulfonium \*\*\*\*\*-\*\* was melted in the 0.07 % of the weight isopropyl alcohol solution of a novolak resin to the resin, and the spin application was carried out on the poly membrane which prepared this previously. It prebaked for 1 minute at 100 degrees C, and the film which consists of two-layer of the layer containing a photo-oxide generating agent and the layer containing an acid propagation agent ] became in thickness of 0.62 micrometers collectively. After exposing ultraviolet rays on this two-layer layer, postbake processing was performed at 100 degrees C, and negatives were developed in 40-degree C ethanol for 1 minute. When asked for the relation between the exposure time and a remaining rate of membrane, having high-sensitivity-ized the two-layer layer which added the acid propagation agent 20 times compared with an additive-free two-layer layer accepted.

[0054] In example 12 example 11, when the completely same exposure as an example 10 was performed about the layer of the two-layer structure which added triphenylsulfonium hexafluoroantimonate instead of triphenylsulfonium \*\*\*\*\*-\*\* as a photo-oxide generating agent, 18 times as many high-sensitivity-ization as this accepted by addition of an acid propagation agent. The photographic sensitivity of the layer of the two-layer structure which added the triphenylsulfonium hexafluoroantimonate prepared in the example 13 example 11, and the layer which added triphenylsulfonium hexafluoroantimonate to the polymer of the example 1 which is a well-known chemistry amplification type photoresist was measured. Consequently, the layer of the two-layer structured type which separates and contains an acid propagation agent showed the 25 times as many high sensitivity as this to the chemistry amplification resist.

[0055]

[Effect of the Invention]

- (1) Since a sensitization speed improves sharply, it can use for a high-sensitivity image formation material.
- (2) combining optical irradiation and heat-treatment -- bridge formation of optical hardening resin -- since luminous efficacy improves sharply, it can use to ultraviolet-rays hardening type coating, ink, a surface coating agent, etc. effectively In the paint film which consists of an optical curing agent which carried out pigment-content powder, although it does not happen at all in that hardening is inadequate or the interior since an optical absorption happens only by the surface layer, according to this invention, hardening can be made perfect by heat-treatment after optical irradiation.
- (3) Since the yield of an acid increases sharply by the acid propagation agent, it can reduce the amount of the photo-oxide generating agent used. Consequently, since light can fully permeate to the interior of a sensitization layer, it is enabled to increase the thickness of a sensitization layer of it sharply.

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[Translation done.]

DOCUMENT-IDENTIFIER: US 5985511 A  
TITLE: Photoresist composition

# BSPP:

The photoresist composition of the present invention comprises an amine compound. The amine compound contributes to control of diffusion of the acid generated due to exposure to the resist film, thereby improving the resolution and resistance to time delay effect of the resist and reducing the PFB dependence. The term "amine compound" used herein means a compound containing a primary, secondary or tertiary amino group, preferably a compound whose total number of carbon atoms is not less than 6. When the amino group is not cyclic, the primary or secondary amine is preferred. When the amino group is cyclic, it is preferred that the nitrogen atom is tertiary. Specifically, a primary or secondary amine represented by the general formula (II):

CCOR:

430/270.1



United States Patent [57]

Patent Number: 5,985,511

Yabu et al.

Date of Patent: Nov. 16, 1999

## PHOTORESIST COMPOSITION

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Field of Search 430/270, 430/271, 430/272

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## ABSTRACT

A positive photoresist composition having excellent various properties (e.g., resolution, resistance to time delay effect, profile, small PFB dependence) as well as excellent sensitivity. The resolution and sensitivity, which comprises a polyimide resin whose thermal stability is particularly good, is particularly good. A solution of a polyimide compound as an acid generator in the composition and an organic solvent having a boiling point of not more than 110 °C is provided.

20 Claims, 30 Drawings

Details Text Image

KWIC

Details Text Image

Full